A Highly Accurate Quartic Force Field and Rovibrational Spectroscopic Constants for the Azirinyl Cation (c-C$_2$NH$_2$$^+$) and Its Isomers

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Abstract

Azirinyl cation is an aromatic cyclic molecule that is isoelectronic with cyclopropenylidene, c-C$_3$H$_2$, and c-C$_3$H$_3$$^+$. Cyclopropenylidene has been shown to be ubiquitous, existing in many different astrophysical environments. Given the similar chemistry between C and N, and the relative abundances between C and N in astrophysical environments, it is expected that there should be aromatic ringed molecules that incorporate N in the ring, but as yet, no such molecule has been identified. To address this issue, the present study uses high levels of electronic structure theory to compute a highly accurate quartic force field (QFF) for azirinyl cation and its two lowest lying isomers, the cyanomethyl and isocyanomethyl cations. The theoretical approach uses the singles and doubles coupled-cluster method that includes a perturbative correction for connected triple excitations, CCSD(T), together with extrapolation to the one-particle basis set limit and corrections for scalar relativity and core-correlation. The QFF is then used in a second-order vibrational perturbation theory analysis (VPT2) to compute the fundamental vibrational frequencies and rovibrational spectroscopic constants for all three C$_2$NH$_2$$^+$ isomers. The reliability of the VPT2 vibrational frequencies is tested by comparison to vibrational configuration interaction (VCI) calculations and excellent agreement is found between the two approaches. Fundamental vibrational frequencies and rovibrational spectroscopic constants for all singly substituted ^{13}C, ^{15}N, and D isotopologues are also reported. It is expected that the highly accurate

spectroscopic data reported herein will be useful in the identification of these cations in high-resolution experimental or astronomical observations.

I.   INTRODUCTION

Cyclopropenylidene, c-C_3H_2, is generally regarded as the smallest aromatic compound that has been identified in astronomical observations.[1] It has been observed in many different astronomical environments including the interstellar medium (ISM), photodissociation regions (PDRs), planetary nebulae, and cicumstellar disks.[2-8] Several of its isotopologues have also been identified in astronomical observations (see Refs. 9 and 10, and references therein)[9,10]. Cyclopropenylidene obeys the Huckel (4n+2) rule where n=0, and it was first identified in matrix isolation laboratory experiments in 1984 with the aid of *ab initio* calculations.[11,12] Astrochemical models suggest that the main precursor to formation of c-C_3H_2 is the molecular cation c-$C_3H_3^+$ through dissociative attachment with an electron.[13,14] Hence astronomers have been trying to identify c-$C_3H_3^+$ in various astrophysical environments for more than 30 years, but because c-$C_3H_3^+$ has no permanent dipole moment, radio astronomy is not an option for the main isotopologue[15-19] ~~(for example, see Refs. 15-19 and references therein)~~.

An interesting question that our group has been investigating in recent years concerns the incorporation of a N atom within cyclic organic astrochemical, which is of interest to the formation of N containing polycyclic aromatic hydrocarbon (PANH) molecules as well as many prebiotic molecules such as pyrimidine and purine.[20-25] However, while a number of N containing molecules have been identified in the ISM or other astrophysical environments, none of these incorporate a N atom within a ring. An obvious possible target would be the analog of cyclopropenylidene. For example, exchanging a N atom for a C-H group in c-C_3H_2 leads to c-C_2NH, for which we have computed a highly accurate quartic force field (QFF), and rovibrational spectroscopic constants.[21,22] One difference between c-C_3H_2 and c-C_2NH, however, is that c-C_2NH is not the lowest energy isomer as the lowest triplet state of quasi-linear HCCN lies 7.8 kcal/mol lower in energy,[21] and has been observed in the ISM.[26] Nevertheless, in keeping with this line of investigation, it is reasonable to consider the c-$C_2NH_2^+$ cation as this would be expected to be the main source of formation for c-C_2NH by analogy with the hydrocarbon species. Additionally, in our previous investigation of this molecule and its isomers, we have shown that unlike the deprotonated isomers, azirinyl cation, c-$C_2NH_2^+$, is indeed the lowest energy isomer (see Ref. 25 and references therein). $C_2NH_2^+$ has three low-lying isomers – as indicated, azirinyl cation is the global minimum, cyanomethyl cation is the second lowest isomer, and the isocyanomethyl cation

is the third lowest isomer on the potential energy surface (PES). See Ref. 25 for more discussion on previous experimental and theoretical studies of the isomers of $C_2NH_2^+$.

Neither the rotational nor rovibrational spectrum of any isomer of $C_2NH_2^+$ has been observed in high resolution, though. Thus, the goal of the present study is to provide highly accurate rovibrational spectroscopic constants and vibrational frequencies for azirinyl cation and its isomers so that they may be used to identify these molecules in either high-resolution laboratory experiments or directly in high-resolution astronomical observations.

The theoretical methods used in the present study are described in the next section, while the results and discussion are presented in the following section. Conclusions are presented in the final section.

II.   METHODS

The isolation of the three $C_2NH_2^+$ isomers on the global PES allows us to study their structure, vibrational spectra, and rovibrational spectroscopic constants via the well-established procedure of second-order vibrational perturbation theory (VPT2) using high quality *ab initio* quartic force fields (QFF). The detailed procedure used here is described in Refs. 27-29, with some recent examples in Refs. 16, 21, 30, and 31. A recent high-resolution experiment has confirmed the reliability and accuracy of our predictions for $C_3H_3^+$.[18] In short, a reference geometry is obtained by correcting the equilibrium structure from the CCSD(T)/cc-pV5Z level of theory with a core-valence correlation correction computed at the CCSD(T)/cc-pCVQZ level of theory. CCSD(T)/cc-pVXZ (*X*=T,Q,5) single point energies computed on a quartic displacement grid are then extrapolated[32] to the complete one-particle basis set limit with a three-point formula. Corrections for scalar-relativity and core-valence correlation are then added to obtain the CcCR (complete basis set limit + core correlation correction + relativistic correction) total composite electronic energy at each grid point.[27-29] The scalar relativistic correction[33,34] is computed at the CCSD(T)/cc-pVTZ-dk level and the core-valence correction is determined as the energy difference between two sets of two-point extrapolated CCSD(T)/cc-pCVXZ (X=T,Q) energies, with and without core-correlation. All electronic structure calculations were performed with the Molpro 2010.1 quantum chemistry program.[35]

The full QFF is determined by a least-squares fit of the CcCR energies, and an accurate minimum energy structure is determined. The QFF is then fit again using the exact minimum energy structure to yield a QFF that has essentially zero gradient terms. The symmetry internal coordinate force constants are transformed into Cartesian derivatives using the INTDER[36] program. A VPT2 analysis is run using the SPECTRO[37] program. In addition, the single point energy datasets for each isomer have been fit to a Morse QFF representation (for the bond stretches), so that the potentials will exhibit correct limiting behavior which is required for variational rovibrational calculations.[38,39]

A depiction of the three $C_2NH_2^+$ isomers included in this study is given in Fig. 1. All three isomers are planar and possess C_{2v} symmetry. The global minimum is Isomer A, azirinyl cation. The three sets of nine symmetry adapted internal coordinates are defined for the three isomers as follows:

Isomer A	Isomer B	Isomer C
$S1(a_1) = R_{C1\text{-}C2}$	$S1(a_1) = (R_{C1\text{-}H1} + R_{C1\text{-}H2})/\sqrt{2}$	$S1(a_1) = (R_{C1\text{-}H1} + R_{C1\text{-}H2})/\sqrt{2}$
$S2(a_1) = (R_{N\text{-}C1} + R_{N\text{-}C2})/\sqrt{2}$	$S2(a_1) = R_{C1\text{-}C2}$	$S2(a_1) = R_{C1\text{-}N}$
$S3(a_1) = (R_{C1\text{-}H1} + R_{C2\text{-}H2})/\sqrt{2}$	$S3(a_1) = R_{C2\text{-}N}$	$S3(a_1) = R_{N\text{-}C2}$
$S4(a_1) = (\angle N\text{-}C1\text{-}H1 + \angle N\text{-}C2\text{-}H2)/\sqrt{2}$	$S4(a_1) = \angle H1\text{-}C1\text{-}H2$	$S4(a_1) = \angle H1\text{-}C1\text{-}H2$
$S5(b_2) = (R_{N\text{-}C1} - R_{N\text{-}C2})/\sqrt{2}$	$S5(b_2) = (R_{C1\text{-}H1} - R_{C1\text{-}H2})/\sqrt{2}$	$S5(b_2) = (R_{C1\text{-}H1} - R_{C1\text{-}H2})/\sqrt{2}$
$S6(b_2) = (R_{C1\text{-}H1} - R_{C2\text{-}H2})/\sqrt{2}$	$S6(b_2) = (\angle H1\text{-}C1\text{-}C2 - \angle H2\text{-}C1\text{-}C2)/\sqrt{2}$	$S6(b_2) = (\angle H1\text{-}C1\text{-}C2 - \angle H2\text{-}C1\text{-}C2)/\sqrt{2}$
$S7(b_2) = (\angle N\text{-}C1\text{-}H1 - \angle N\text{-}C2\text{-}H2)/\sqrt{2}$	$S7(b_2) = LIN1(C1\text{-}C2\text{-}N)$ in plane	$S7(b_2) = LIN1(C1\text{-}N\text{-}C2)$ in plane
$S8(b_1) = (\tau_{H1\text{-}C1\text{-}N\text{-}C2} - \tau_{H2\text{-}C2\text{-}N\text{-}C1})/\sqrt{2}$	$S8(b_1) = LIN1(C1\text{-}C2\text{-}N)$ out of plane	$S8(b_1) = LIN1(C1\text{-}N\text{-}C2)$ out of plane
$S9(a_2) = (\tau_{H1\text{-}C1\text{-}N\text{-}C2} + \tau_{H2\text{-}C2\text{-}N\text{-}C1})/\sqrt{2}$	$S9(b_1) = \tau_{H1\text{-}C1\text{-}N\text{-}H2}$	$S9(b_1) = \tau_{H1\text{-}C1\text{-}C2\text{-}H2}$

where τ represents torsional angles for isomer A and using the terminal atoms, i.e. N for isomer B and C2 for isomer C. The step sizes (one Δ) used for bond length and angle related coordinates are 0.005 Å/rad, which we have found yields a good balance between eliminating higher-order contamination and providing enough significant digits in the energies. For Isomer A, the quartic displacement grid of 880 symmetry-unique geometries was set up around the reference geometry. The 880 final energies are converted to a 1585 symmetry-redundant energy set for the least-squares fit procedure. The sum of the squared residuals was 0.722E-16 E_h^2. In the Morse-representation refit, the sum of the squared residuals is 8.0E-18 E_h^2 In the Morse-representation used here, all angle related coordinates S4 and S7-S9 remain unchanged. The QFFs constructed here for azirinyl cation follow the conventions used previously for $c\text{-}C_3H_2$.[40]

Similarly, high-quality QFFs are computed in a similar way for Isomers B and C. They both have C_{2v} symmetry, but their terminal C and N atoms are exchanged. A linear bending coordinate is required along C-C-N or C-N-C, and thus the four LIN1 coordinates for isomers B and C are linear bending coordinates. For Isomers B and C, the step sizes used are 0.005 Å/rad or better for S1-S5, and 0.025 Å/rad for S6-S9, as tests showed these performed well. In total, CcCR single point energies were computed for 931 symmetry unique geometries, which expand to the full set of 1613 redundant geometries for the least square's fits. The sum of the squared residuals is 1.1~1.2E-16 E_h^2 For the Morse representation refit for variational calculations, coordinates S4 and S6-S9 did not change similar to the procedure for Isomer A, and the sum of the squared residuals are 0.98 – 1.47E-17 $E_h.^2$

The variational vibrational calculations are carried out using the MULTIMODE (MM) program, which has been described in detail elsewhere.[41-43] In short, the Watson Hamiltonian in mass-scaled normal mode coordinates forms the basis of MM. A key feature of MM is the hierarchical n-mode representation (nMR) of the potential. We have tested the convergence improvement from 3MR to 4MR and 5MR. 26 primitive harmonic-oscillator basis functions are included with 16 Gauss-Hermite integration points for each mode. The maximum quanta for single mode are tested from 8 to 11. The convergence should be within ~1-2 cm^{-1} for vibrational fundamentals.

III.   RESULTS AND DISCUSSIONS

In Figure 1 we report the equilibrium structures of the three isomers: azirinyl A, cyanomethyl B, and isocyanomethyl cations C, as well as the vibrationally averaged structures for the main isotopologues. In Table 1 we report the vibrationally averaged geometries, rotational constants, vibrational fundamentals, and selected spectroscopic constants of the three Isomers. Note, that the vibrational modes are sorted by the symmetry of vibration and numbered in order of decreasing harmonic frequency, as is traditionally done. Additionally, the most important symmetry internal coordinates are specified. The MM fundamentals and zero-point energies (ZPEs) are reported in parentheses, next to the VPT2 values. A benefit of our high-quality QFF + VPT2 analysis is that the isotopic substitution effects on geometries, vibrational fundamentals and spectroscopic constants can be easily determined. Vibrationally averaged rotational constants and

fundamental vibrational frequencies for all ^{15}N, ^{13}C or D singly substituted isotopologues are reported in Table 2, and the full set of vibrationally averaged geometries and selected spectroscopic constants are presented in the supplementary information. The full set of symmetry internal coordinate quadratic, cubic, and quartic force constants (i.e., the full QFFs) for each isomer are also given in the supplementary material. In absence of any experimentally measured infrared spectra, a direct comparison of vibrational spectra computed from the *ab initio* QFF + VPT2 is not possible, but interesting details of the results are discussed in the following sections for each isomer.

Azirinyl cation (A)

The structures and harmonic vibrational frequencies of the azirinyl cation have been extensively explored in an earlier work by Kokkila et al.[25], and we will not duplicate their efforts here. We see from Table 1 and Fig. 1a that the geometries change very little from equilibrium to the zero-point vibrationally averaged structure. The CN distances vary by 0.006Å, the CH distance by approximately +/-0.003Å, and the CNC angle by +/-0.01°. This agreement between the vibrationally zero-point averaged structure and the equilibrium structure shows that there are no large amplitude motions amongst the fundamental vibrations. In absence of any floppy vibrational modes, the three-membered cyclic azirinyl cation is not expected to show any unusual anharmonicity effects. Also, the differences between the final equilibrium structure and the reference structure used to set up the QFF grid are even smaller by one more order of magnitude, giving us confidence that the geometry grid used to generate the QFF is reliable.

In Table 1a we report the vibrationally averaged geometry, harmonic and fundamental vibrational frequencies, vibration-rotation constants, centrifugal distortion constants and zero-point vibrational energies of the azirinyl cation. The vibrational modes are arranged in the symmetry order A_1, B_2, B_1, A_2, for the main isotopologues, where A_1 and B_2 represent in-plane vibrational modes. The largest effect of anharmonicity, 139.6 cm^{-1} is seen in the symmetric stretch of the two CH bonds (ν_1). The second largest anharmonicity occurs for the antisymmetric stretching (ν_5) mode and is 136.5 cm^{-1}. The effect of anharmonicity for the three heavy atom stretching modes ν_2, ν_3, and ν_6 is small to moderate; 36.8, 37.4, and 29.4 cm^{-1}, respectively. For the vibrational fundamentals of azirinyl cation, the agreement between VPT2 and MM is excellent, i.e. less than 1 cm^{-1} for ν_1-ν_6, and 1-2 cm^{-1} for ν_7-ν_9. This is slightly better than what we usually

expect from VPT2/MM comparisons. A VCI-suitable Morse-representation of the QFF requires that the θ_{NCH} angles be adopted for S4 and S7, instead of θ_{HCC} which is only ~20° from linearity, which is why the θ_{NCH} angles were used. The vibration-rotation constants of the ν_4, and ν_5-ν_9 modes are affected by Coriollis resonances as indicated in Table 1a). The first overtone of ν_2 is nearly degenerate with the ν_1 fundamental and is therefore as a Type I Fermi resonance for the main isotopologue.

The VPT2 analysis has been performed for the ^{13}C, ^{15}N and D substituted isotopologues of the azirinyl cation using the same QFF. In Table 2a, the vibrationally averaged rotational constants and vibrational fundamentals of $H^{13}C$-N-CH, $H^{13}C$-N-^{13}CH, DC-N-CH, DC-N-CD, and HC-^{15}N-CH isotologues of the azirinyl cation are presented. They are sorted in order of decreasing fundamental frequencies. The symmetry of the various fundamentals has not been indicated because it will be different for different isotopologues, two of which have C_s symmetry and three of which have C_{2v} symmetry, similar to the main isotopologue. There is a significant range in the values of the vibrationally averaged rotational constants, indicating that the rotational spectra for the various isotopologues will be well separated. For example, the A_0 constant ranges from a high of 38172 MHz to a low of 35436 MHz. For the fundamental vibrational frequencies, the largest effect is of course for the C-D stretch when D replaces H, going from just above 3100 cm^{-1} to around 2400 cm^{-1}. The changes for the other fundamentals are large enough to be distinguishable from each other as well as the main isotopologue, though, especially for high-resolution rovibrational experiments.

The high accuracy rovibrational spectroscopic data reported here for azirinyl cation and its isotopologues should be useful in the future identification of these species in either high-resolution laboratory experiments or astronomical observations, similar to our previous study on c-$C_3H_3^+$.[16,18] To elaborate on this point, in 2011 Huang et al.[16] published a QFF (using the same procedures outlined in the current study) and rovibrational spectroscopic analysis of the linear and cyclic forms of $C_3H_3^+$, much like the three isomers included in this study. Their purpose was to aid the interpretation of future experimental and astronomical high-resolution observations, and thus far only one rovibrational band for c-$C_3H_3^+$ has been observed and analyzed.[18] Zhao et al. indicate that they would not have been able to assign the υ_4 band of c-$C_3H_3^+$ without the highly-accurate spectroscopic data published by Huang et al., and indeed the purely ab initio data were very accurate with the band center being off by only 0.55 cm^{-1}, and the rotational constants B_0, C_0, B_4,

and C_4 being off by 9, 4, 9, and 1 MHz, respectively. Another example of the high-accuracy of rovibrational spectroscopic constants obtained using the same procedures as used in the current study is contained in the study on H_2O by Huang and Lee,[27] where the errors for the fundamental vibrational frequencies is 2.68, 1.06, and 2.09 cm^{-1}, respectively, and for the three rotational constants the errors are -798, -355, and 481 MHz, respectively. The errors in the rotational constants for the H_2O molecule are larger than those for c-$C_3H_3^+$, but are more typical of what this level of theory yields, including that usually the error for A_0 is larger than that for B_0 or C_0, whose errors are typically similar. By now, we have used this composite scheme to compute QFFs and rovibrational spectroscopic constants for dozens of molecules and typically fundamental vibrational frequencies are with about 5 cm^{-1} of experiment and errors for rotational constants typically range from ~100 MHz to several hundred MHz, although for quasi-linear molecules these errors can be larger, especially for the A_0 constant. The interested reader is referred to the review of Fortenberry and Lee,[44] and references therein for more information on how the composite QFF scheme used in the current study generally performs.

Cyanomethyl cation (B)

The C_{2v} symmetry $^1A_1$ cyanomethyl cation has its equilibrium structure and vibrationally averaged geometry for the main isotopologue presented in Fig. 1b. The CH distances change only by +0.0073Å, the CC distance by +0.0006Å, and the CN distance by -0.0011Å due to vibrational averaging. The HCH angle increases by 0.23º. Again, the differences between the reference geometry and the final QFF equilibrium structure are about an order of magnitude smaller, indicating that the grid used for the QFF should be reliable. The fact that the vibrational averaging effects are small for the geometrical parameters indicates that at least none of the totally symmetric vibrations exhibit a large amplitude motion.

The vibrationally averaged geometry, harmonic and fundamental vibrational frequencies, vibration-rotation constants, centrifugal distortion constants and zero-point vibrational energies of the cyanomethyl cation, Isomer B, are presented in Table 1b. The anharmonicity is most pronounced for the symmetric and antisymmetric CH stretching modes, as is expected. The anharmonicities for the heavy atom stretches is also in line with expectations. The two linear-bending coordinates, v_7 and v_9, occur at low energies, 312 and 243 cm^{-1}, respectively, but their anharmonic corrections are not that large, approximately +10 cm^{-1}, suggesting that VPT2 should

be reliable, and indeed the agreement between VPT2 and MM is excellent for those two vibrational modes. It is interesting to note that the anharmonic corrections are positive, though, which occurs sometimes for low energy modes. However, note that for Isomer B, overall agreement between VPT2 and MM is less satisfactory relative to Isomer A, but still fairly reasonable. Most differences are less than 5 cm^{-1}, except that the Δ(MM-VPT2) differences for ν_1 and ν_8 are as large as 6-8 cm^{-1}. At least for ν_1, the symmetric CH stretch, this discrepancy may be due to a resonance with $2\nu_3$. This suggests the uncertainty associated with ν_1 could be larger than for the other fundamentals, though we note that the VCI value is most likely more reliable. For ν_8, the Δ(MM-VPT2) difference is slightly larger but using a different representation for the S9 angle coordinate may bring the MM value lower and into better agreement. Note that in our previous l-C$_3$H$_3^+$ QFF/VPT2/VCI work[16], using very similar coordinate definitions yielded a similar level of agreement between VPT2 and MM.

The vibrationally averaged rotational constants A_0, B_0, C_0 and the vibrational fundamentals of the D, ^{13}C, and ^{15}N substituted cyanomethyl cation were calculated by the VPT2 analysis. The computed constants of H$_2$-^{13}CCN, H$_2$C^{13}CN, H$_2$CC^{15}N, HDCCN and DDCCN are presented in Table 2b. The supplementary material to this paper contains selected spectroscopic constants for the isotoplogues of cyanomethyl cation contained in Table 2b. The highly accurate rovibrational spectroscopic constants and fundamental vibrational frequencies presented here for cyanomethyl cation and its isotopologues should be useful in assigning high-resolution experimental data or high-resolution astronomical observations.

Isocyanomethyl cation (C)

Like the other two isomers, the C$_{2v}$ isocyanomethyl cation also exhibits relatively minor differences between its equilibrium and vibrationally averaged structure as shown in Fig. 1c. Again, this indicates that at least the totally symmetric vibrations are not large amplitude motions. The vibrationally averaged CH bond lengths increase by only 0.0082 Å, the CN distance decreases by 0.0001Å, and the NC bond distance decreases by 0.0019Å. The HCH bond angle increases by 0.17° due to vibrational averaging.

The vibrationally averaged geometry, harmonic and fundamental vibrational frequencies, vibration-rotation constants, centrifugal distortion constants and zero-point vibrational energies of the isocyanomethyl cation, Isomer C, are presented in Table 1c. The anharmonicity of the CH stretches and the heavy atom stretches fall in the expected range, similar to Isomers A and B. The lowest energy vibrations are again ν_7 and ν_9, at 237 and 208 cm^{-1}, respectively. In this case, the anharmonic corrections for these linear-bending modes are somewhat larger than found for Isomer B, 16.5 and 20.1 cm^{-1}, respectively, and again they are found to be positive. Even so, it appears that VPT2 is performing well for these vibrational modes as the agreement between VPT2 and MM is excellent, with differences less than 1.5 cm^{-1} for both fundamentals. In general, the agreement between VPT2 and MM for the fundamental vibrational frequencies mirrors that found for Isomer B, with the largest differences occurring for ν_1 (6.3 cm^{-1}) and ν_8 (7.1 cm^{-1}), and the differences for all of the other vibrations being less than 3 cm^{-1} except for ν_3, which is 3.3 cm^{-1}. The possible explanation for the Δ(MM-VPT2) difference for the symmetric CH stretch ν_1 of Isomer C is the same as for Isomer B, as this mode is in resonance with $2\nu_3$, and thus the VCI value is most likely more reliable.

A great advantage of our high quality QFF + VPT2 analysis is that isotopic substitution effects can be easily determined. For convenience, Table 2c summarizes the vibrationally averaged rotational constants, vibrational fundamentals, and zero-point energies, of all ^{15}N, ^{13}C or D singly substituted isotopologues from VPT2 analysis. Specifically, the isotopologues included are: H_2-^{13}CNC, H_2CN^{13}C, H_2C^{15}NC, HDCNC and DDCNC.

In the supplementary material, the related harmonic frequencies, quartic/sextic centrifugal distortion constants, vibrationally averaged bond length/angles, rotational constants are reported for both the vibrational ground state and the 9 fundamentals; and ro-vibrational spectra, and microwave spectra are also reported. In the following section we discuss simulated spectra for Isomers A, B, and C.

Simulated Spectra with IR Intensities

The double harmonic approximation infrared (IR) intensities of each isomer, computed at the MP2/cc-pVTZ level of theory, are included in Table 1. In order to assess which vibrational modes may represent the easiest target for experimental or astronomical observation, we have plotted the spectra of the main isotopologue for all three isomers in Figure 2. It is immediately

apparent that the ν_2 vibration (the terminal NC stretch) for isocyanomethyl cation is far and away the most intense band from any of the three isomers. For cyanomethyl cation, the most intense band is similarly the terminal CN stretch, also ν_2 for Isomer B. The most intense band for azirinyl cation is the antisymmetric CH stretch, ν_5, and this is in fact the most intense CH stretch band for any of the three isomers. All three isomers have bands that should be observable in an astronomical observation, but which band is targeted might depend on the observatory. For example, using the Echelon-Cross-Echelle Spectrograph (EXES) instrument on the Stratospheric Observatory for Infrared Astronomy (SOFIA), the only band for azirinyl cation that might be observable is ν_6, since ν_5 is outside the range of EXES,[45,46] whereas the most intense bands for both the cyanomethyl and isocyanomethyl cations fall within the range that EXES can target. In any case, the simulated spectra given in Fig. 2 should aid experimentalist and astronomers to identify which vibrational bands should be most easily observed.

In addition, we carried out purely rotational microwave spectral simulations of azirinyl cation and its isomers at 50K, using the PGOPHER program[47] with the ab initio dipole moment (2.79D for azirinyl, 5.21D for cyanomethyl, and 4.07 for isocyanomethyl),[25] vibrationally averaged rotational constants, and centrifugal distortion constants computed for the three isomers at their local minima structure. See Fig.3 a-c for the high-resolution rotational structure. For the main isotopologue A, intense lines are between 3 cm^{-1} and 30 cm^{-1}, with a maximum around 10-20 cm^{-1}. The spectra for isomers B and C look similar, and peak between 8-12 cm^{-1}. The Isomer B transitions are stronger than those of Isomer C, which is probably because Isomer B has a larger dipole moment.[25] Overview rovibrational simulations for all of the fundamentals at 50K are included in the supplementary material. The 200K rotational and rovibrational spectral simulations are also available in the supplementary materials, where the MW peak positions move up to around 35 cm^{-1}. We believe these spectra may facilitate the future identification of azirinyl isomers, and help distinguish them.

IV. **Conclusions**

Highly accurate QFFs have been computed for the three most stable isomers of $C_2NH_2^+$, the azirinyl, cyanomethyl, and isocyanomethyl cations. These were computed using the CCSD(T) electronic structure method together with the Dunning cc-pVXZ (X=T, Q, 5) one-particle basis sets and included extrapolation to the one-particle basis set limit and corrections for scalar

relativity and core-correlation. The QFFs were then used in a VPT2 analysis to obtain fundamental vibrational frequencies, vibrationally averaged rotational constants and geometrical parameters, vibration-rotation constants, and quartic and sextic centrifugal distortion constants. The reliability of VPT2 was tested by also computing the fundamental vibrational frequencies using the variational vibrational CI MM method. Agreement between the VCI and VPT2 fundamentals for the semirigid azirinyl cation is excellent, indicating that the VPT2 method should also yield reliable spectroscopic constants. For the cyanomethyl and isocyanomethyl cations, the agreement between VCI and VPT2 for the fundamental vibrational frequencies was also excellent except for two modes where the difference was between 6-8 cm^{-1}. It is likely that the difference for at least one of the modes is due to a strong Fermi resonance. Nonetheless, it is concluded that the VPT2 spectroscopic constants for both the cyanomethyl and isocyanomethyl cations should also be very reliable. We expect that the highly accurate rovibrational spectroscopic data presented here will be useful in assigning either experimental or astronomical high-resolution spectroscopic observations, using something like the EXES instrument on SOFIA. However, we note that all three isomers possess large dipole moments, 2.79, 5.21, and 4.07 D for the azirinyl, cyanomethyl, and isocyanomethyl cations, respectively.[25] Thus, the highly accurate vibrationally averaged rotational constants and quartic centrifugal distortion constants could be used to assign a purely rotational spectrum from the Atacama Large Millimeter Array (ALMA) as well. Finally, we note that the azirinyl cation is isoelectronic to cyclopropenylidene, c-C_3H_2, and c-$C_3H_3^+$, and if identified in an astronomical observation would be the first such aromatic molecule with a N atom incorporated in the ring structure.

Supporting Information

Rovibrational spectroscopic constants, quadratic, cubic, and quartic force constants, VPT2 constants of the isotopolgues, and simulated rovibrational spectra at 50K and 200K of the azirinyl ion, and its two isomers are presented in the supplementary information file available electronically via web.

Acknowledgements

Tables

Table 1. $C_2H_2N^+$ vibrationally averaged structure parameters (Å/°), harmonic frequencies (with intensities in parenthesis, MP2/cc-pVTZ) and vibrational fundamentals (cm^{-1}), and rotational constants (MHz), vibration-rotation constants (MHz) and quartic centrifugal distortion constants (MHz) computed on our best CCSD(T) QFF (3pt-extrapolated + rel + core), with resonances included.

a)

Isomer A	R_{CN} 1.34009	θ_{CNC} 60.282°$\quad$ R_{CC} 1.34579	A_{eq}	38777.2	B_{eq}	30760.3	C_{eq}	17153.3
Azirinyl	R_{CH} 1.08425	θ_{HCC} 158.904°$\quad$ θ_{HCN} 141.237°	A_0	38579.3	B_0	30552.4	C_0	17001.6

	Harmonic cm^{-1}	Fundamental cm^{-1} VPT2 (VCI)	Vib-Rot constants (MHz) α^a	α^b	α^c	Centrifugal Distortion Constants (MHz)				
ν_1 (a_1) S3	3282.8(23.7)	3143.2$^\$$ (3143.4)	31.5	157.1	54.9	τ_{aaaa}	-0.653	D_J	0.023
ν_2 (a_1) S1	1664.9(6.5)	1628.1$^\$$ (1628.6)	99.5	119.3	55.4	τ_{bbbb}	-0.243	D_{JK}	0.101
ν_3 (a_1) S2	1386.0(9.0)	1348.6 (1348.7)	-70.1	56.0	-66.1	τ_{cccc}	-0.032	D_K	0.039
ν_4 (a_1) S4	946.2(0.1)	925.6 (925.2)	-77.0*	45.5	64.7	τ_{aabb}	-0.404	d_1	-0.013
ν_5 (b_2) S6	3234.8(199.5)	3098.3 (3098.0)	32.5	145.7	50.5	τ_{aacc}	-0.086	d_2	-0.006
ν_6 (b_2) S5	1176.8(31.2)	1147.4 (1147.7)	292.2*	-75.3	172.8	τ_{bbcc}	-0.050		
ν_7 (b_2) S7	1001.2(0.0)	977.3 (976.0)	-41.8*	-28.6*	11.9				
ν_8 (b_1) S8	860.8(21.1)	844.2 (842.9)	138.6*	6.3*	-24.9				
ν_9 (a_2) S9	1012.3(0.0)	989.3 (987.3)	-9.6*	-10.1	-15.5				
ZPE		7196.6 (7192.7)							

$^\$$ affected by Fermi resonances; * affected by Coriolis resonances.

b)

Isomer B	R_{C-H} 1.09544 Å	θ_{HCH} 120.758°	A_{eq}	280854.5	B_{eq}	10361.1	C_{eq}	9992.4
Cyanomethylene	R_{C-C} 1.36667 Å$\quad$ R_{C-N} 1.17633 Å	θ_{HCC} 119.621°	A_0	277137.4	B_0	10372.5	C_0	9987.8

	Harmonic cm^{-1}	Fundamental cm^{-1} VPT2 (VCI-5MR)	Vib-Rot constants (MHz) α^a	α^b	α^c	Centrifugal Distortion Constants (MHz)				
ν_1 (a_1) S1	3102.1(39.4)	2992.3$^\$$ (2984.6)	4902.3	8.1	13.8	τ_{aaaa}	-81.758	D_J	0.004
ν_2 (a_1) S3	2181.7(186.6)	2127.2$^\$$ (2128.7)	143.6	68.2	63.4	τ_{bbbb}	-0.016	D_{JK}	0.519
ν_3 (a_1) S4	1467.9(7.0)	1445.0 (1440.3)	-3134.7	-22.1	12.9	τ_{cccc}	-0.014	D_K	19.916
ν_4 (a_1) S2	1092.8(77.1)	1087.9 (1086.5)	276.5	6.6	32.1*	τ_{aabb}	-2.092	d_1	-0.0001
ν_5 (b_2) S5	3219.5(83.5)	3073.6$^\$$ (3074.0)	3246.8	9.7	11.2	τ_{aacc}	-0.013	d_2	-0.00005
ν_6 (b_2) S6	1035.3(0.6)	1014.2 (1016.0)	-8079.0*	-10.1	7.4*	τ_{bbcc}	-0.015		
ν_7 (b_2) S7	311.5(1.1)	321.9 (321.9)	1112.8*	-62.8	-29.2				
ν_8 (b_1) S9	1087.8(6.4)	1074.4 (1080.5)	829.1*	49.8	-7.9				
ν_9 (b_1) S8	242.8(0.4)	253.0 (253.4)	8136.9*	-70.5	-94.5				
ZPE		6811.3 (6797.7)							

$^\$$ polyad treatments $\quad$ * affected by Coriolis resonances.

c)

Isomer C Isocyanomethylene	R_{HC} 1.09608 Å R_{CN} 1.28112 Å R_{NC} 1.21531 Å	θ_{HCH} 122.109° θ_{HCN} 118.946°	A_{eq} A_0	277122.0 272982.0	B_{eq} B_0	11594.5 11613.6	C_0 C_{eq}	11128.9 11127.6

	Harmonic cm⁻¹	Fundamental cm⁻¹ VPT2 (VCI)	Vib-Rot constants (MHz)			Centrifugal Distortion Constants (MHz)		
			α^a	α^b	α^c			
ν_1 (a_1) S1	3096.0(18.9)	2907.6$^\$$(2913.9)	4771.4	8.2	15.0	τ_{aaaa} -73.566	D_J	0.004
ν_2 (a_1) S3	2033.4(729.2)	1985.9 (1986.8)	248.0	82.6	76.2	τ_{bbbb} -0.019	D_{JK}	0.772
ν_3 (a_1) S4	1519.7(11.3)	1480.6$^\$$ (1477.3)	-2686.1	-25.1	18.9	τ_{cccc} -0.016	D_K	17.615
ν_4 (a_1) S2	1213.7(9.1)	1199.2$^\$$(1198.0)	153.6	29.2	15.1	τ_{aabb} -3.094	d_1	-0.0002
ν_5 (b_2) S5	3223.9(56.4)	3068.1$^\$$(3070.5)	3165.6	10.1	11.9	τ_{aacc} -0.025	d_2	-0.00009
ν_6 (b_2) S6	1155.9(8.3)	1133.4 (1135.3)	-5827.0*	-5.0	33.3	τ_{bbcc} -0.017		
ν_7 (b_2) S7	220.6(1.9)	237.1 (236.4)	359.1*	-94.6	-41.2			
ν_8 (b_1) S9	1138.8(6.1)	1122.6 (1129.7)	2046.8*	38.2	-5.5			
ν_9 (b_1) S8	187.6(8.7)	207.7 (206.4)	6048.8*	-81.8	-121.0			
ZPE		6827.7 (6817.2)						

$^\$$ polyad treatments, the other state in ν_1 polyad is $2\nu_3$ at 3001.0 cm⁻¹ (VPT2) or 2991.8 cm⁻¹ (VCI) * affected by Coriolis resonances.

Table 2: Vibrationally averaged rotational constants (MHz) and vibrational fundamentals (cm⁻¹) of ¹³C, ¹⁵N and D substituted isotopologues, estimated by VPT2 (SPECTRO) analysis, sorted by decreasing fundamental frequency order.

(a)

Isomer A	H¹³C-N-CH	H¹³C-N-¹³CH	DC-N-CH	DC-N-CD	HC-¹⁵N-CH
A_0	38172.03	37736.03	37610.72	35435.67	36920.21
B_0	29584.54	28831.37	25707.61	22598.37	30395.59
C_0	16620.44	16298.85	15229.32	13763.20	16624.05
ν_1	3134.94	3123.91	3117.10	2436.75	3143.39
ν_2	3092.19	3088.02	2379.64	2312.88	3100.17
ν_3	1608.04	1586.82	1578.01	1513.93	1620.01
ν_4	1334.75	1319.94	1335.55	1319.00	1335.35
ν_5	1132.80	1119.21	1134.22	1124.00	1136.51
ν_6	982.95	976.36	954.37	814.89	997.03
ν_7	973.78	970.43	945.17	771.26	976.10
ν_8	925.26	924.88	723.75	681.59	923.45
ν_9	842.06	840.16	699.86	640.79	850.48
ZPE (VPT2)	7157.60	7118.42	6555.30	5912.74	7180.15

(b)

Isomer B	H₂-¹³CCN	H₂C-¹³CN	H₂CC-¹⁵N	HD-CCN	D₂-CCN
A_0	273886.96	273880.72	273893.74	189651.01	138073.73
B_0	10037.84	10359.90	10039.57	9708.34	9175.97
C_0	9675.00	9973.97	9676.57	9224.30	8595.70

ν_1	3061.32	3067.79	3072.17	3031.17	2324.87
ν_2	2984.24	2992.23	2991.95	2254.17	2206.65
ν_3	2165.01	2082.14	2105.13	2122.58	2097.24
ν_4	1435.70	1444.65	1444.16	1321.80	1193.18
ν_5	1069.06	1084.35	1073.48	1071.90	933.21
ν_6	1069.56	1073.07	1076.61	958.76	831.19
ν_7	1007.23	1008.73	1014.10	857.68	825.27
ν_8	321.73	315.17	319.86	302.86	288.71
ν_9	251.52	246.56	251.77	249.78	247.51
ZPE (VPT2)	6778.59	6772.72	6791.41	6187.49	5556.82

(c)

Isomer C	H_2-^{13}CNC	H_2CN-^{13}C	H_2C-^{15}NC	HD-CNC	D_2-CNC
A_0	269818.54	269823.61	269818.16	186939.18	136021.67
B_0	11258.22	11162.26	11598.76	10880.74	10294.54
C_0	10798.46	10710.01	11111.45	10269.42	9561.24
ν_1	3058.05	3064.36	3095.90	3029.40	2333.56
ν_2	2908.14	2918.73	2920.16	2244.89	2192.36
ν_3	1980.15	1966.93	1946.35	1974.69	1966.01
ν_4	1477.09	1485.75	1487.62	1381.62	1279.93
ν_5	1183.61	1182.37	1198.37	1186.27	991.32
ν_6	1126.17	1133.62	1130.41	999.79	896.52
ν_7	1117.15	1121.96	1122.30	930.22	866.71
ν_8	236.93	235.22	232.97	225.45	216.72
ν_9	206.76	206.58	203.58	205.24	203.41
ZPE (VPT2)	6796.68	6808.87	6804.15	6195.45	5550.23

Figure 1. Equilibrium geometries (top) and vibrationally averaged geometries (bottom; main isotopologue) for the azirinyl (a), cyanomethyl (b) and isocyanomethyl (c) cations.
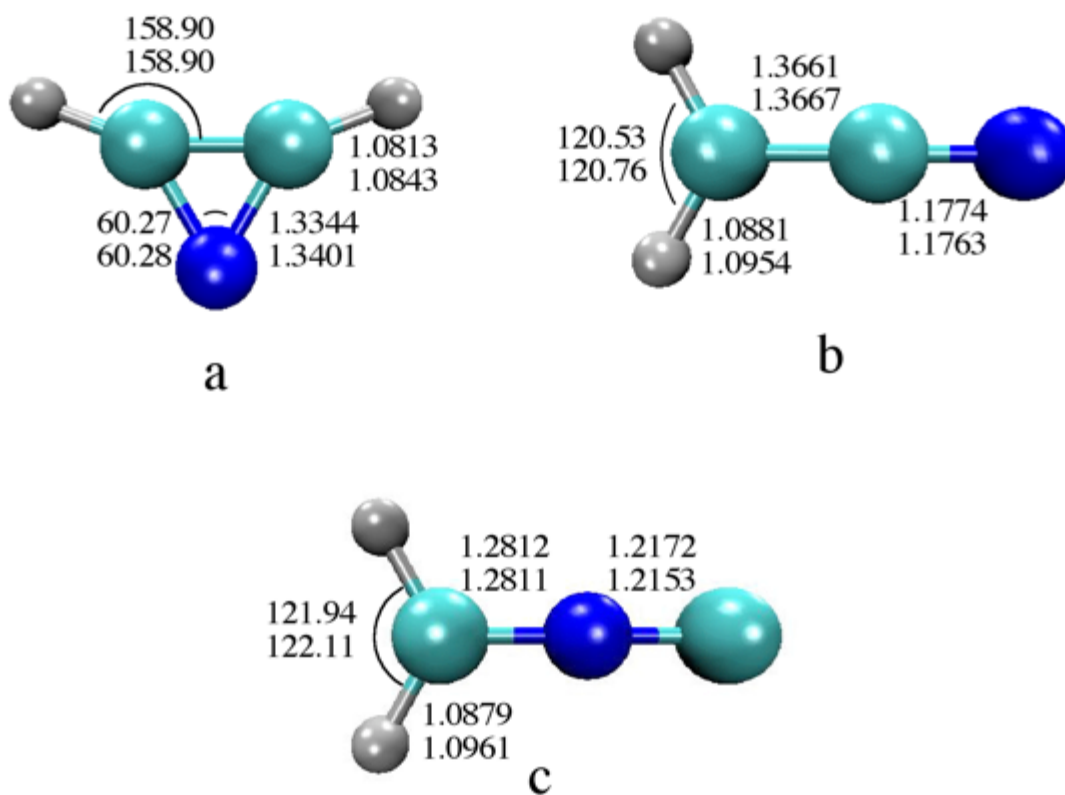

a

b

c

Figure 2. Simulated stick IR spectrum of the main isotopologues of the azirinyl, cyanomethyl and isocyanomethyl cations using the fundamental vibrational frequencies together with double harmonic IR intensities (all from Table 1).
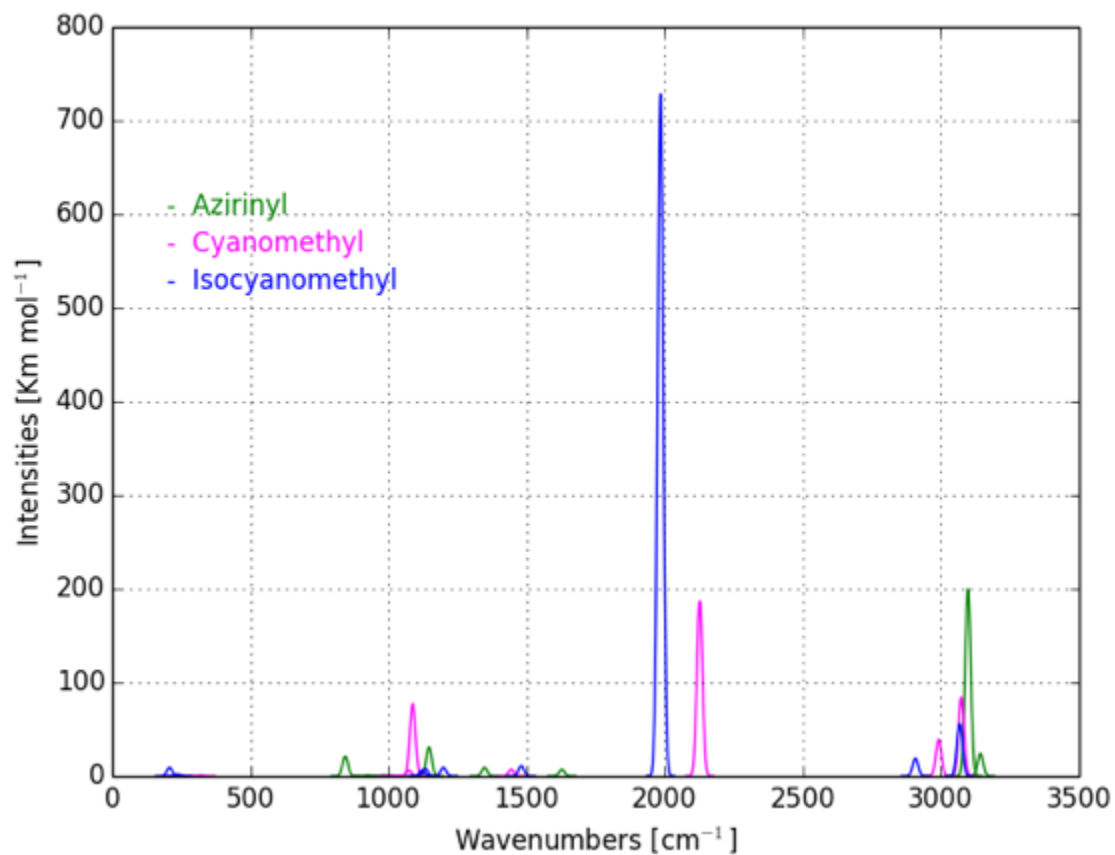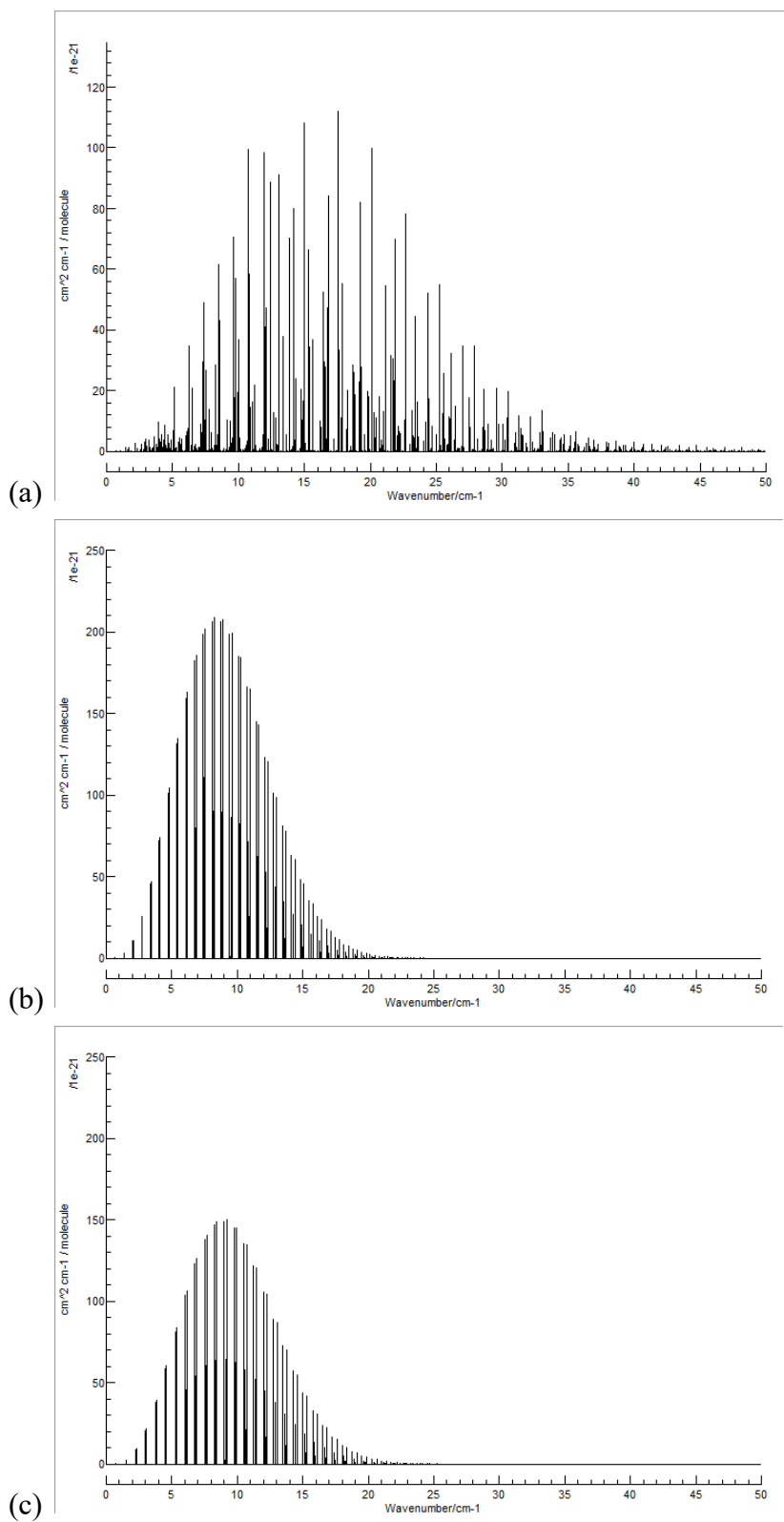
Fig.3 The 50K microwave spectra of: (a) isomer A; (b) isomer B; (c) isomer C.

(a)

(b)

(c)

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